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Theory of rotational transitions in molecular collisions

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It is a very great pleasure for me to have the opportunity to give a talk at this symposium in honour of the centenary celebration of Indian Association for the Cultivation of Science. I hope the institute will continue to serve not only as an Indian centre but also as a world centre of atomic and molecular physics.

The present talk is concerned with one of the recent topics of the theory of molecular collisions : the calculation of the cross section for rotational transitions in collisions between molecules. In the last ten years, a great number of papers have been published of collisions between atoms and molecules, while very few works have been reported on molecule-molecule systems (Secrest 1973). In principle, there is no difference between the theories on the two systems. In practice, however, the complexities of a problem in molecule-molecule collisions and the numerical work required to solve it increase by several orders of magnitudes as compared with those in atom-molecule collisions. Sometimes it is undertaken to represent one of the colliding molecules by a structureless particle and reduce the problem to a simpler atom-molecule collision. In this treatment, one of the molecules is assumed to stay in its ground rotational state. In a real molecular gas, however, a simultaneous transitions in rotational states of both molecules are quite important. In other words, the rotational-rotational energy transfer play an important role in macroscopic phenomena. This and other effects may give rise to somewhat qualitative distinction between atom-molecule and molecule-molecule collisions.

Rotational level spacings of a molecule are of the order of meV or less. When a molecule encounters another molecule, a rotational transition is induced with a high probability, unless the collision energy is extremely low. Thus, the rotational energy transfer is a very common process in many fields. To see the importance of the study of the rotational excitation in molecular encounters, here are shown a few examples to which the knowledge about the rotational excitation is immediately applicable.

The first example of the phenomena in which the rotational transition plays a part is the transport phenomena in a molecular gas (Gordon 1973). It is well known that the existence of internal degrees of freedom such as rotational motion can affect transport coefficients like thermal conductivity and viscosity. Under normal conditions, the rotational transition has but a small effect. The rotational

B. *Semiclassical (classical S-matrix)*

To overcome the above disadvanages in the classical calculation, the classical S-matrix theory has been developed (Miller 1974). In this method, a problem is formulated in action angle variables, which correspond to the quantum numbers in quantum mechanics. Once the relevant classical trajectories are computed, a classical analogue of S-matrix is calculated with the use of the correspondence principle. Then the cross section is obtained from the S-matrix in the same manner as in quantum mechanics. In this way, an interference effect can be included. To take into account a tunnelling process, a complex-valued trajectory is introduced to link the classically forbidden states. This method of classical S-matrix, which is, in essence, a new kind of semiclassical approach, is now successfully used to improve the classical calculations.

C. *Semiclassical (traditional)*

There is a more traditional semiclassical method. Here, as in the methods A and B, the translational motion is treated in classical mechanics, but a quantum-mechanical description is used for the internal states. In this method, we often assume the same classical path for all the internal states. That assumption requires both for the translational energy and for the relative orbital angular momentum to be slightly changed during a collision.

D. *Quantum-mechanical*

Finally comes the quantum-mechanical calculations. There are a large number of approximate methods applicable to the rotational cross section calculation. Let me consider here only the most accurate one, the close-coupling method. Suppose a collision between two heteronuclear diatomic molecules. The wave function of the whole system can be expanded in terms of the rotational wave functions ϕ_α :

$$\psi = \sum_\alpha f_\alpha \psi_\alpha .$$

Here α species the rotational states of the molecules and stands for the four quantum numbers $(J_1 M_1 J_2 M_2)$; J_i and M_i are the rotational angular momentum and its projection of i-th molecule. The coefficient f_α describes the relative motion of the colliding molecules and satisfies the equation

$$L_\alpha f_\alpha = \sum_{\alpha'} < \alpha \mid V \mid \alpha' > f_{\alpha'} ,$$

where L_α is an operator involving the kinetic energy and centrifugal force and $< \alpha \mid V \mid \alpha' >$ implies the element of the interaction matrix. In the close-coupling method, the summation over α' is truncated to a finite number of terms and the resulting coupled equations are solved numerically. The accuracy of this method depends on the number of internal states included. Now we estimate

the dimensionarity of the coupled equations. For the sake of illustration, we consider a transition from the ground rotational state and restrict the excitation up to the state, at most, $J=J_{max}$ for both molecules. Since each J-state has $(2J+1)$ substates, the total number of the states to be coupled is calculated as

$$N = \sum_{J_1=0}^{J_{max}} \sum_{J_2=0}^{J_{max}} (2J_1+1)(2J_2+1) = (J_{max}+1)^4.$$

At room temperature, most molecules have the order of ten or more rotational states significantly populated. Even when J_{max} is as small as ten, the dimension of the coupled equations becomes enormously large so that it is practically impossible to solve them. Thus, the application of the close-coupling method as it stands is restricted to a few exceptional cases, unless an extremely efficient method is developed to solve the coupled differential quations. In fact, the quantum-mechanical close-coupling method has been applied so far only to the simplest case, the collision of hydrogen molecules (Green 1975).

Recently several attempts have been made to reduce the dimensionarity of the coupled equations. They are called the effective Hamiltonian methods and involve various types of angular momentum decouplings. In the following two of them are introduced.

In many practical cases, we do not need any information about the direction of the rotational angular momentum of a molecule. That is, we do not need to know the dependence of the cross section on the magnetic quantum numbers M. In 1972, Rabitz (1972) proposed a method, called effective potential method, in which he eliminated the M-dependence of the coupled equations by taking a kind of orientation-averaging procedure. In his formulation, the rotational states of the molecules are specified only by J_1 and J_2. He derived an effective potential which couples those J-states. The number of coupled states is just the product of the numbers of J_1-states and J_2-states. In the last -mentioned example, it becomes

$$N = (J_{max}+1)^2.$$

Thus a great reduction is realized in the labour needed to solve the coupled quations.

Another attempt is McGuire and Kouri's coupled-state or j_z-conserving method (McGuire and Kouri 1974). They assume some kind of restriction to the change in the relative orbital angular momentum during a collission. This assumption results in the conservation of M or the z-component of the rotational angular momentum of colliding molecules. The coupled equations can be solved separately for each M. The numerical effort required to solve the equations lies somewhere between those for the Rabitz method and for the rigorous treatment of the close-coupling scheme.

In the last three years, these effective Hamiltonian methods have been applied to a large number of systems. Most of them are atom-molecule collisions, but a few calculations have been done for collisions between molecules. Brief outlines of two of them are given below for an illustration. They may serve also as typical examples of rotational cross section calculations for molecular collisions.

The first one is the collision of two hydrogen molecules. Zarur and Rabitz (1974) considered the process

$$H_2(J_1)+H_2(J_2)\rightarrow H_2(J_1')+H_2(J_2')$$

They included rotational states from $J=0$ to 6 for each molecule and solved numerically the quantum-mechanical coupled equations adapted to the effective potential method. The interaction potential was assumed to have the form

$$V = V_0(R)[1+0.14\{P_2(\cos\chi_1)+P_2(\cos\chi_2)\}],$$

where V_0 is the spherically symmetric part of the potential and determined experimentally. The anisotropy parameter has been chosen so as to give the best fit to the SCF potential. In some calculations, they added to this potential the interaction between the molecular quadrupoles to check the effect of the long-range anisotropy of the interaction. Their calculation gives many interesting results. For instance, the rotational excitation cross section is found to be enhanced when the projectile molecule is in its rotationally excited state. Hence, the treatment in which one of the molecules is regarded as a structureless and spherical particle underestimates the excitation cross section.

The second example is the calculation of the probability of the rotational transition in the collision of two nitrogen molecules (Itikawa 1975). The calculations is performed in the conventional semiclassical framework. First, the trajectory of the relative motion is determined classically. Then, the amplitude of the transition is calculated by solving a set of coupled differential equations which are derived from the time-dependent Schrödinger equation. To reduce the dimensionarity of the coupled equations, use is made of the effective potential method of Rabitz (1972). The resulting equations are solved in the exponential approximation (Takayanagi 1954). Thus the transition probability for the process

$$N_2(J_1)+N_2(J_2)\rightarrow N_2(J_1')+N_2(J_2')$$

is given by

$$P(J_1J_2\rightarrow J_1'J_2') = |\langle J_1'J_2'|\exp K|J_1J_2\rangle|^2.$$

Here K is a matrix whose element is defined by

$$\langle J_a\, J_b\,|K|\,J_c\, J_d\rangle = (i\hbar)^{-1}\int_{-\infty}^{\infty} dt\,\langle J_a\, J_b\,|V^{eff}[R(t)]\,|J_c\, J_d\rangle \times\exp(i(W_a+W_b-W_c-W_d)/\hbar),$$

where W is the rotational energy and $R(t)$ is the relative distance of the two molecules at time t. The matrix element of the effective potential $< J_a\ J_b \mid V^{eff} \mid J_c\ J_d >$ is derived from the exact one $<J_aM_aJ_bM_b \mid V \mid J_cM_cJ_dM_d>$ by using Rabitz's procedure. In this way, we can consider couplings among all of the states connected through the selection rules and the energy balance. In the actual calculation, $R(t)$ is determined by solving the classical equation of motion in the modified-wave number approximation (Takayangi 1954).

For the interaction between the nitrogen molecules, the potential model

$$V = C\exp(-\alpha R)[1+A\{P_2(\cos\chi_1)+P_2(\cos\chi_2)\} +BP_2(\cos\chi_1)P_2(\cos\chi_2)]-C_6/R^6$$

is adopted. The potential parameters C, C_6 and α are estimated from molecular-beam experiments and an analysis of transport coefficients. The anisotropy parameters A and B are left adjustable. This form of the potential model enables an analytical computation of the elements of the K matrix. Once we give the initial values of the relative kinetic energy and the rotational angular momenta of the molecules, we can compute the transition probabilities for all the energetically possible final states at the same time. By using those transition probabilities, which are given as functions of an impact parameter, the rotational cross section can be easily obtained. For further details of the calculation and the results, the original paper (Itikawa 1975) should be referred.

Unfortunately, we can not compare these theoretical cross sections directly with experimental data. There is no cross section measured for any rotational transition in molecule-molecule collisions. We can use, however, these theoretical values to analyse macroscopic phenomena. Rabitz and Lam (1975) calculated rotational relaxation times by using their cross sections for hydrogen molecules. The result can be compared with the relaxation time obtained in various experimental methods. The primary object of the calculation for N_2+N_2 is the application of the resulting transition probabilities to the study of the shock structure of a nitrogen gas. That work is now under way with the use of the Monte Carlo technique (Yoshikawa and Itikawa 1976).

As described above, rather comprehensive studies have just begun of the rotational transitions in molecule-molecule collisions. There are many things yet to be done. To apply to the studies on macroscopic phenomena, we have to develop much more efficient but at least qualitatively reliable methods of cross section calculation. In those studies, the cross section calculation is not the ultimate goal but just one step to the goal. Another important task in the future is to find out some general trends in the dependence of the cross section on initial rotational states, collision energy, types of interaction potential, and so on. Any of such

systematics, if found, must be very useful in understanding the role of the rotational transition in various problems.

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